ETHYLENE GLYCOL IN WASTE WATER

Arizona Department of Health Services
Division of State Laboratory Services

Analytical Method

Analyte: Ethylene Glycol Method No.: BLS-188

Matrix: Waste Water Working Range: 2.0 to 50 mg/L

Procedure: Direct injection on gas chromatograph equipped with Flame ionization detector.

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1. METHOD REFERENCE

1.1 There are no technical papers or procedures available at this time.

Acknowledgments

(i) Mr. Puczkewyz of Department of Health Services, Connecticut.

(ii) Supelco technical assistance.

2 SYNOPSIS

2.1 Direct injection of waste water is made into gas chromatograph equipped with flame ionization detector for ethylene glycol determination.

2.2 This method can also be used to Propylene Glycol determination.

3. RANGES, SENSITIVITY, DETECTION LIMIT

3.1 The normal working range for this analyte is 1.0 mg/L to 50 mg/L. Reporting levels are at 2.0 mg/L.

4. INTERFERENCES

4.1 Due to lack of experience in the analysis of varying matrices, no interferences have been determined at this time.

5. SAMPLE HANDLING, PRESERVATION AND HOLDING TIME

5.1 Sampling will be done in a teflon sealed amber bottle. (40 ml VOA bottles can be used)

5.2 Samples must be refrigerated after sampling on route to the laboratory and by the laboratory until the analysis.

5.3 There is no established holding period for this analyte in waste water. We recommend a 2 week holding time from the time of sampling.

6. APPARATUS

6.1 Hewlett - Packard 5880A gas chromatograph with a flame ionization detector or equivalent and connected to Hewlett - Packard integrating Printer/Plotter or a data system.

6.2 Auto sampler HP-7671 A with 10 ul syringe adjusted to 2 ul volume.

6.3 Column: 6 ft x 2 mm glass or glass lined, Carbopack C 0.8% Theed, 80/100 mesh. (Supelco Cat No. 1-1880).

6.4 Hamilton syringes, assorted sizes.

6.5 Assorted volumetric flasks and pipets.

6.6 1 ml mini-vials and caps (red septa, crimp cap).

6.7 Crimper for 1 ml mini-vials and caps.

7. REAGENTS

7.1 Ethylene Glycol

A. Primary standard: J.T. Baker (# L718-07).
B. Secondary standard: Aldrich (#10,246-6).

7.2 Prepurified nitrogen carrier gas.

7.3 Prepurified hydrogen.

7.4 Compressed air.

7.5 Deionized water.

7.6 HMDS (Hexamethyldisilazane, Supelco)

8. STANDARDS PREPARATION

NOTE: Standards are prepared volumetrically.

8.1 Intermediate Primary Standard

Dilute 1 gram of neat ethylene glycol to 100 mls with D.I. water.

8.2 Primary Working Standards

Prepare working standards from intermediate standards as follows or as appropriate.

ul of Intermediate standard diluted to 100 ml of D.I. water	**ng/ul of Working standard**
10	1.0
50	5.0
100	10.0
200	20.0
500	50.0

Calculations:

a. Intermediate Standard

1 gram of ethylene glycol to 100 mls of D.I. will give.

$$\frac{\textbf{1.0 g}}{\textbf{100 mls}} = \textbf{10.0 mg/ml}$$

b. Working Standard

10 ul of 10.0 mg/ml (ug/ul) to 100 ml of D.I. water will give.

$$\frac{10 \text{ ul} \times 10.0 \text{ ug/ul}}{100 \text{ mls}} = 1.0 \text{ ug/ml or } 1.0 \text{ ng/ul.}$$

8.3 Control Standard (Secondary Source)

Control Standards can be prepared in the similar manner as Primary Standards. Prepare control working standard at 10.0 ng/ul or an appropriate level.

9. SAMPLE PREPARATION

9.1 Preparation of Spike samples

9.1.1 To 10 mls of the sample, add 10 ul of intermediate standard (10.0 mg/ml) to give 10 ppm spike level.

9.2 Preparation of the Samples

9.2.1 No sample preparation is required. All samples must be at room temperature before analysis. 1-2 ul of the samples are injected directly into the gas chromatograph and analyzed.

9.2.2 If autosampler is being used, transfer about 1 ml of the samples to the mini vials and inject 1-2 ul.

10. INSTRUMENT PREPARATION

10.1 Initial Setup Conditions

NOTE: The following instrumental preparation is for HP 5880 A instrument only. The appropriate procedures have to be followed for individual instruments.

HP 5880A gas chromatograph with 2 integrating printer/plotter terminals.

Detectors: 2 flame ionization detectors: Detectors A and B.

NOTE: The following gas parameters were found to be optimal for our gas chromatograph. The parameters might vary for other gas chromatographs.

Regulator Pressures on gas tanks

	1st Stage	2nd Stage
Hydrogen	>500 PSI	55 PSI
Compressed Air	>500 PSI	75 PSI
Nitrogen (Carrier for FID)	>500 PSI	60 PSI

Gas Flows

Air	~380 -400 mls/min
Hydrogen	~ 40 mls/min
Nitrogen - carrier A/B	~ 20 mls/min

Note: Hydrogen flow is critical in optimizing the detector.

Temperatures:

Detector Port	200 degrees C.
Injector Port	200 degrees C.
Oven Temp	110 degrees C isothermal.
Run Time	10-12 minutes
Post Run, Column Temp	120 degrees C for 3 minutes (to bake off the water).

Modifications are made, as necessary, to obtain the best separation of eluting peaks.

10.2 Daily Operating Procedure

Change septa on injection port(s) to be used.

On terminal 1: Press (LIST) (ENTER). Compare parameters listed to initial setup conditions. When applicable change those parameters which differ to match initial setup values.

If instrument lists non-applicable calibration curve, press (DELETE) (CALIB). Terminal will respond "delete all". (1=yes) (ENTER).

To list "Run Table," Press (LIST), (YELLOW KEY), (RUN TBL) and (ENTER)

To delete a run time: (DELETE), (RUN TIME), time to be deleted, (STOP) and (ENTER)

To enter a run time, (RUN TIME), key in time, (STOP), and (ENTER)

To view or to modify a report table: Press (LIST), (YELLOW KEY), (REPORT TBL) and (ENTER).

To change Signal: Press (SIGNAL) (A) or (B) (ENTER), whichever is appropriate.

Set attenuation by pressing <2>, (NUMBER) (usually 0 for terminal 1 and 4 for terminal 2) (ENTER).

Open gas tank on/off valve for hydrogen and compressed air.

On front panel of HP 5880 A, check carrier gas regulator flow (~20).

Screw open, air and hydrogen on/off valves for side A and/or side B. Depress FID ignitor toggle switch ("man") for side A and/or B. Listen for small popping noise of flame being ignited. Release toggle switch. Check for flame with a mirror (condensate collect on mirror surface).

Allow detector and flame to stabilize 10 to 15 minutes.

Enter sample table: (Yellow Key), (Auto SEQ), and (ENTER).
Enter position, (ENTER) sample identification and (ENTER).
To exit sample table: press (EXIT), (ENTER)

Change injection ports: (Edit), (Auto Seq), a comma, the desired port (1 = port A and 2 = port B) and (ENTER).

To start auto sequence (Start), (Auto Seq), the starting position, a comma, the ending position, and (ENTER).

10.3 Shut Down Procedure

Shut off air and H2 flows on front panel of G.C.

11. SAMPLES ANALYSIS

11.1 Auto sampler

Refer to Instrument Preparation Section 10 for sample table and how to start analysis.

General guidelines for order of analysis:

Reagent blank (D.I. water)

Standards

Control

Sample

Spike

Control

NOTE: Controls are run after every 5 samples.

12. CALCULATIONS

12.1 A linear regression for an external standard, multi-level calibration method as outlined in the instruction manual for 5880, is used to calculate the sample concentrations. No corrections are needed if the volume injections are normalized to 1 or 2 ul.

12.2 Results are reported as mg/L.

12.3 Some criteria for reporting results:

1. For samples that have between 1 and 2 mg/L, report as "Trace <2 mg/L."
2. Report the concentration found for samples that have 2 or >2 mg/L.
3. For samples that have <1 mg/L, report as "None Detected, <1 mg/L."

13. QUALITY ASSURANCE

13.1 The standards must be made up fresh with each run. All sample concentrations are bracketed by standards.

13.2 The standard curve consists of no less than 3 standards, not including the blank.

13.3 10% of all the samples, or 1 sample per batch, whichever is greater will be spiked. Acceptable spike recoveries are at 100 ± 20%. Report any deviations to sample submitter.

13.4 10% of all the samples, or 1 sample per batch, whichever is greater will be analyzed in duplicate.

13.5 Include controls at 10% of the samples or 1 per batch, whichever is greater. Acceptable control levels are 100 ± 10%.

13.6 Additional washes and flushes of the autosampler syringe are needed to avoid carryover. (For e.g., 10 washes and flushes instead of 5 washes and flushes).

13.7 At present, no suitable internal standard has been found. Retention time of the water peak can be used for relative retention time of ethylene glycol.

13.8 At present, no suitable secondary column, for confirmation, has been found. Porapak QS, (Aldrich Cat # 2720), can achieve a 50 mg/L detection limit, and should be used for ethylene glycol concentrations above this limit.

13.9 Periodic replacement of the glass wool at the front end of the column is needed to maintain the uniform response.

13.10 See Appendix A, for the instructions to pack "Theed" Column.

14. PRECISION AND ACCURACY

14.1 2 Waste waters A & B were selected for this study.

Waste water A was subdivided into 10 subsamples. 5 subsamples were spiked at 11 ppm each and the other 5 subsamples were spiked at 22 ppm each.

Waste water B was also treated similarly. Waste waters A and B did not contain any background Ethylene glycol. The following are the results obtained for the spike recoveries.

Waste Water	Spike level	Spike recovery %	Average Spike Recovery
Sample A	11 ppm each	78,77,76,76,75	76%
Sample A	22 ppm each	81,81,80,79,80	80%
Sample B	11 ppm each	95,95,96,97,96	96%
Sample B	22 ppm each	95,95,95,96,96	95%

14.2 Controls were prepared from a secondary source at 11 ppm. Average control recoveries were at 97%.

APPENDIX A

Instructions to Pack a "Theed" Column.

1. Use glass or glass-lined column. A stainless steel column is not suitable.

2. Rinse the column with acetone followed by petroleum ether. Blow dry with clean air or N2. Work in hood.

3. Silanize with Hexamethyldisilanzane (HMDS) by wetting the column with about 0.5 - 1.0 ml of HMDS. Blow off the excess HMDS with air or N2.

(CAUTION: HMDS IS AN IRRITANT AND IS EXTREMELY FLAMMABLE!)

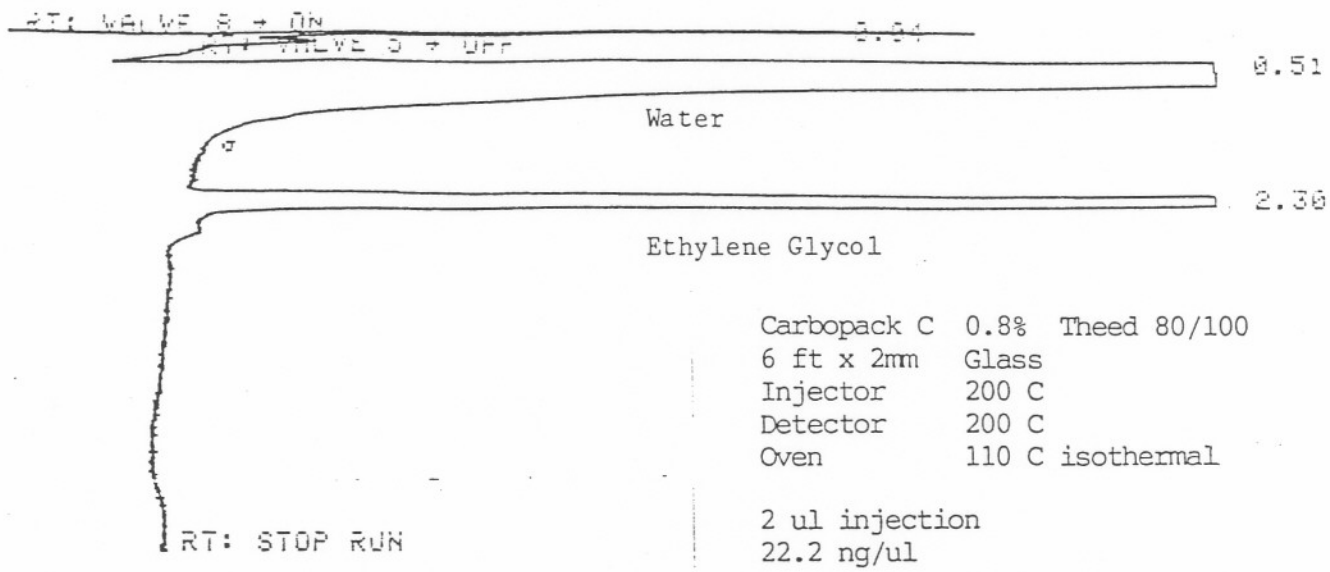
4. Pack the column with "Theed" packing material. Leave about 6 inches of blank space at the front and back ends of the column. (The blank space will prevent bleed of liquid phase of the column packing. The maximum temperature of the column packing is 120 degrees C and the injector and detector port temperatures are at 200 degrees C). Use silanized glass wool to plug the ends.

5. Condition the column, overnight at 120 degrees C.

APPENDIX B

(Ethylene Glycol Chromatograms)

Ethylene Glycol on Carbopack C
(Primary Column)



Carbopack C 0.8% Theed 80/100
6 ft x 2mm Glass
Injector 200 C
Detector 200 C
Oven 110 C isothermal

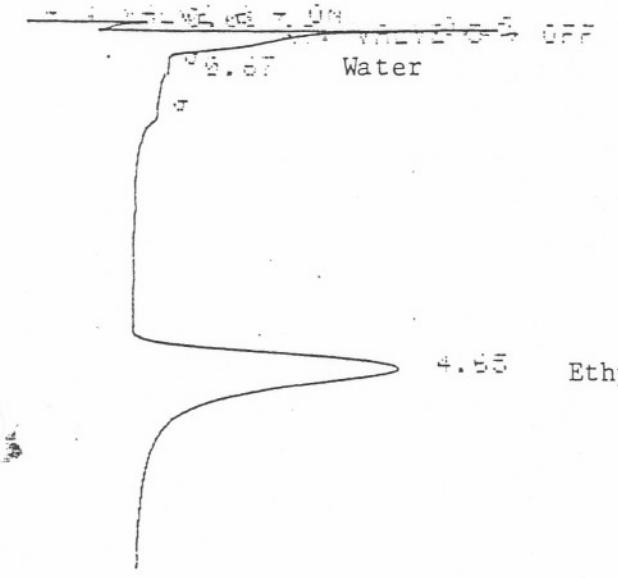
2 ul injection
22.2 ng/ul

HP 5880A SAMPLER INJECTION @ 12:40
SAMPLE # : ID CODE :
9 17743.SP2
AREA %

RT	AREA	TYPE	WIDTH	HEIGHT	BASELINE	AREA %
0.00			BASELINE @ START RUN = 35.20			
0.00			THRESHOLD @ START RUN = 1			
0.00			PEAK WIDTH @ START RUN = 0.16			
0.04	22.37	BV	0.038	9.14	35.18	1.703
0.51	1040.36	BV	SYM\	59.71	35.06	79.171
2.30	251.34	BB	0.113	34.98	35.90	19.127

TOTAL AREA = 1314.08
MULTIPLIER = 1

Ethylene Glycol on Porapak QS
(Confirmatory Column)



Porapak QS	100/120	4 ft x 2mm
Injector	300 C	
Detector	300 C	
Oven	160 C isothermal	

3 ul injection
111 ng/ul

[illegible] MANUAL INJECTION @ 12:26 JAN 30, 1990
AREA %

RT	AREA	TYPE	WIDTH	HEIGHT	BASELINE	AREA %
0.00			BASELINE @ START RUN = 36.65			
0.00			THRESHOLD @ START RUN = 1			
0.00			PEAK WIDTH @ START RUN = 0.10			
0.01	4.50	BP	-----	0.24	36.05	0.175
0.15	591.31	PV	------*	64.64	26.07	23.015
4.00	1974.03	BB	0.546*	56.42	32.27	76.810